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ION CYCLE AND FOREST ECOSYSTEM STABILITY

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ABSTRACT

On the base of a thermodynamical forest ecosystem model, stability is defined as the system being in quasi-steady state. The steady state is defined by the balance between ion uptake (phytomass production) and ion mineralization (secondary production) and by the balance between input and output. In steady state the ion cycle of the system is closed. A discoupling (opening) of the ion cycle leads to a net production or consumption of protons. This causes changes in the chemical soil environment of the organisms. In this context resilience is defined as the ability of the system to maintain the H^+/OH^- balance. The buffering mechanisms operating in soils and organisms are partially reviewed, as critical parameters buffer rates are identified. The natural climatic variation, the necessity to reestablish continously system elements, and the biomass utilization by man lead to a discoupling of the ion cycle and produce thus chemical stress. A sequence of ecosystem states is described: aggradation phase, stability with high resilience, humus disintergration, stability with low resilience, build up of decomposer refuge, and podzolization. From the data known about rates of proton loading and proton buffering it must be concluded that acid deposition forces forest ecosystems from the stability ranges into the destabilization phases (transition states), even at low rates of deposition.

Definition of the forest ecosystem

A system can be described by its elements and the interaction between them. In ecosystems the system elements are organisms like plants, animals and microorganisms, but also structural units like ecological niches or like the soil type and the humus-form. Also the structural units building up organisms are system elements, the smallest unit of structural units to be considered as system elements are the binding forms of chemical elements.

In respect to the border lines to neighbouring ecosystems, the principle applied in defining forest ecosystems is that of homogeneity: If we consider a plant association existing on a special soil association, this ecosystem touches another ecosystem if the plant or soil association is changing. In respect to long lasting stability, reproduction of species is an indispensable feature of ecosystems. The various stages of reproduction are therefore part of the homogeneous forest ecosystem. This seems strange if one considers even-aged forests, but it is an essential requirement for an ecosystem. In a stable even-aged forest ecosystem, the different age classes represent different stages in a strictly cyclic development.

The border line between ecosystem and atmosphere follows the plant and soil surfaces. The border line to the lithosphere should be drawn at the surface of soil minerals in such a way that the surface bound material (ions and organic matter) belongs to the ecosystem, whereas the silicate lattice belongs to the lithosphere and thus to the environment of the ecosystem. This means that the cation release by silicate weathering is treated as an input into the ecosystem.

A forest ecosystem model

Ecosystems are open systems, that means they exchange matter and energy with their environment. Systems of this kind are treated in the thermodynamics of irreversible processes. If we look for appropriate ecosystem models, we should therefore look in this field of science. According to PRIGOGINE (1947), open systems in steady state organize themselves according to

the principle of minimizing entropy production. It seems strange that this principle should apply to ecosystems which utilize only a few percent of radiation energy input for photosynthesis. But one has to realize that around 40 % of the energy input are used for transpiration, that is for transportation, and the rest is used for heat regulation. This model has received already some attention and it seems worthwhile to develop it further. It is subjected to limitations, however: a steady state is in principle unachievable due to the inconstancy of the environment (variability of the climate, change of the lithosphere by weathering processes) and due to the inconstancy of the system elements (the system elements have a limited life duration and must be replaced continuously). The fact that forest ecosystems have been stable for millions of years (e.g. in the tropics since teriary age, with the restrictions that species composition changed due to evolution and due to changes in the lithosphere caused by weathering) points to the fact, however, that forest ecosystems can approach a steady state very closely: so close that we would'nt be able to detect the difference by the methods available. We may therefore say that forest ecosystems can reach a quasi-steady state.

The ion cycle in the ecosystem in steady state

All processes included in ion turnover can be reduced to four fluxes: input (e.g. from atmosphere, or by weathering of soil minerals), output (e.g. leaching, denitrification), uptake from soil solution into biomass (by plants and microorganisms), and release of ions during decomposition (mineralization). We consider an ecosystem in which input and output are equal for each element. For such an ecosystem, quasi-steady state can be achieved: in the temporal and spatial mean all stores in the system are constant. This covers phytomass, total biomass, soil organic matter, the various chemical elements and their various binding forms. In such an ecosystem the rate of assimilation must be equal to the rate of respiration, or, if one includes also the turnover of elements other than C, H and O, the rate of phytomass production must be equal to the rate of mineralization:

$$CO_2 + H_2O + X^+Y^- \underset{\text{mineralization}}{\overset{\text{phytomass production}}{\rightleftharpoons}} CH_2OX^+Y^- + O_2$$

In eq. 1, X^+Y^- symbolyzes the cations and anions of the elements other than C, H and O; they are taken up from the soil solution and return during mineralization again to the soil solution.

To account for the ionic status, the precursor of the ions present in soil solution and the binding form in the plant must be known. As binding forms in the soil matrix and in the plant are assumed:

N: only organic binding forms with charge zero; fixed or exchangeable NH_4^+ in soil as well as NO_3^- in plant are neglected

Na, K, Mg, Ca, Mn, Al, Fe: as cations, the charge is balanced by inorganic or organic anions

S, P, Cl: as anions balanced by cations. This is an oversimplification in case of S (S containing amino acids), but the error introduced can be neglected for the following consideration. In case of P, the pyrophospate bound creates dissociating OH groups during its breakdown.

With the exception of N assimilation and denitrification, the input and output of all elements occurs in ionic form. The precursor of assimilated N is uncharged N_2, the reaction products of denitrification are also uncharged compounds (N_2, N_2O).

The ion cycle within the ecosystem can be reduced to two processes: ion uptake and ion mineralization. As the following equations show, these processes are connected with proton production (H^+) and consumption (OH^-), respectively:

nitrogen: $$R\text{-}NH_2 + H_2O \underset{\text{uptake}}{\overset{\text{mineralization}}{\rightleftharpoons}} R\text{-}OH + NH_3 \begin{cases} \nearrow NH_4^+ + OH^- \\ \searrow NO_3^- + H^+ \end{cases}$$

sulfur: $$R\text{-}SH + H_2O \underset{\text{uptake}}{\overset{\text{mineralization}}{\rightleftharpoons}} R\text{-}OH + H_2S \rightarrow SO_4^{2-} + 2H^+$$

phosphorus: $$R\text{-}O\text{-}PO(OH)_2 + H_2O \underset{\text{uptake}}{\overset{\text{mineralization}}{\rightleftharpoons}} R\text{-}OH + PO_4^{3-} + 3H^+$$

Cations: $$\left[R\text{-}C\begin{matrix}=O\\ O^-\end{matrix}\right]_2 Ca + 2H_2O \underset{\text{uptake}}{\overset{\text{mineralization}}{\rightleftharpoons}} 2R\text{-}H + CO_2 + Ca^{2+} + 2OH^-$$

If the N accumulated in the plants stems from N_2 (after assimilation) or soil organic N (after mineralization), its transfer to plant organic N is not connected with any net change in charge neither in soil nor in plant, that means it is not connected with any net proton transfer.

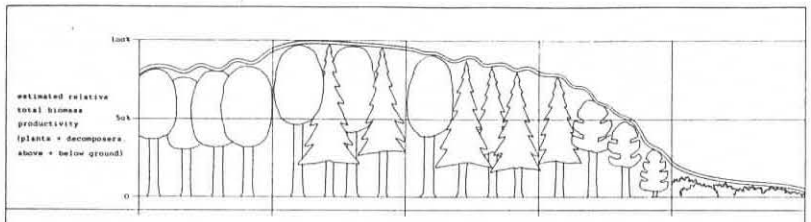
In steady state ion uptake and ion mineralization balance each other. This means that in steady state no net proton turnover occurs in the system. It is clear, however, that ion uptake and ion mineralization do'nt occur in the ecosystem always at the same place and with the same rate. This means that not only the retention and disposition of nutrients, but also the buffering of H^+/OH^- ions determines the resilience of the ecosystem. In both respects the main weight of buffering lies on the soil - he is the reaction vessel of the ecosystem. If the organisms become involved in buffering, their buffer abilities vary a great deal (determining tolerance) and adverse consequences are likely to appear (e.g. growth reductions, damages: plastic strain).

The ion cycle in the ecosystem is controlled by the following principles:

- mass conservation. From this principle it follows that mass balances are a proper way to check steady state conditions and to follow changes of the ecosystem.
- maintenance of electrical neutrality in the flux. From this principle it follows that cation/anion balances of fluxes are a proper way to measure transfers.
- tendency to maintain the H^+/OH^- balance in the compartments (root, plant, soil, mineral soil, organic top layer). From this principle it follows that the net proton production or consumption in a compartment may be a critical variable to realize changes in the ecosystem. The net proton turnover in a compartment can be calculated from the cation/anion balance of the storage changes in this compartment.

Resilience in respect to the ion cycle

The central aspect of resilience is the H^+/OH^- balance of the compartments of the ecosystem. This statement rests on the



Soil buffering regions and plant growth

pH_{ESS}	8.6	8.2	5.0	4.2	3.8	3.0
buffer region	carbonic acid/carbonate	carbonic acid/silicate	strong acid/exchanger	strong acid /Al-oxide		strong acid/Fe-oxide
proton donator proton source	H_2CO_3 root and decomposer respiration		HNO_3 nitrification	HCl NH_4^+ uptake	H_2SO_4 SO_2 emission	R-COOH organic matter
buffer reaction	$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^-$	$CaAl_2Si_2O_8 + 2H_2CO_3 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- + Al_2Si_2O_5(OH)_4$ Ca feldspar Kaolinite	$n[AlOOH + 0.5H^+ + H_2O] \rightarrow [Al(OH)_{2.5}^{0.5+}]_n + 0.5nH_2O$ clay	$AlOOH + 3H^+ \rightarrow Al^{3+} + 2H_2O$		$FeOOH + 3H^+ \rightarrow Fe^{3+} + 2H_2O$
composition of soil solution	high concentration of Ca^{2+} and HCO_3^-	low concentration of Ca^{2+}, Mg^{2+}, K^+ and HCO_3^-	Varying concentration of NO_3^-, Cl^- and/or SO_4^{2-} Ca^{2+}; Mg^{2+}; K^+; $[Al(OH)_{2.5}^{0.5+}]_n$	Al^{3+}		Fe^{3+}
cation exchange capacity	$CEC_e = CEC_t$	$CEC_e/CEC_t > 0.8$	$0.8 > CEC_e/CEC_t > 0.1$			
buffer capacity per ha and dm soil depth	150 kmol H^+ per 1 % $CaCO_3$	25 kmol H^+ per 1 % silicate	7 kmol H^+ per 1 % clay	150 kmol H^+ per 1 % clay		
buffer rate per ha and year	> 2 kmol H^+	0.2 - 2 kmol H^+	small (< 0.2 kmol H^+ ?)	large as long as $[Al(OH)_{2.5}^{0.5+}]_n$ is available, otherwise small		> 2 kmol H^+
leaching of nutrients	mainly Ca^{2+}	very limited	leaching of exchangeable Ca^{2+}, Mg^{2+}, K^+	leaching complete		
composition of exchangeable cations	Ca^{2+} dominating	balanced	$[Al(OH)_{2.5}^{0.5+}]_n$ dominating	Al^{3+} dominating		Fe^{3+} and H^+ dominating
Humusform	Mull	Mull and Mull-like Moder	typical moder	rawhumus-like moder		rawhumus
cation/anion balance in plant uptake	anion surplus	balanced	cation surplus	large cation surplus		ion uptake ceases
limitations for plant growth	small limitation by wide Ca^{2+}/K^+ ration and anion surplus in uptake	no limitations by chemical soil factors	suffering of non-tolerant plants by Al-toxicity exclusion of calcicole species	suffering of all plants by Al-toxicity reduction of growth in calcifuge species including beech.		suffering of all plants by Al-Fe-toxicity only plants rooting in top organic layer survive

Figure 1.

knowledge that changes in the chemical soil state influences binding forms, stores and turnover rates of nutrients to a great deal.

Plants and decomposers produce CO_2 by respiration at a high rate. If no other bases or acids are available, the ecosystem approaches therefore the chemical state of the system H_2O/CO_2 at CO_2 pressures close to or above that of air. Such systems will achieve pH values between 5.0 and 5.6. pH values in the liquid phase of ecosystems in this range indicate therefore the absence of soluble bases or acids, that means they indicate the neutrality range of the ecosystem. This neutrality range can be expected to be the optimal state which is possible in the ecosphere. Optimal means that this state allows a maximal diversity both for producers (plants) and for decomposers. At pH values above 5.6 basicity is accumulated, e.g. in the form of bicarbonates or carbonates. This can take place in soil or in plant. At pH values below 5.0 acidity is accumulated. In the pH range between 5 and 3, which is characteristic for acid soils, mineral acidity exists as cation acids. The most relevant cation acids are ionic species of manganese, aluminium, iron and heavy metals. Some of them act as micronutrients, but all are toxic at low concentrations. The toxicity depends not only on the kind of the chemical element, but also on the kind of ion species of the same element. A better understanding of cation acid toxicity (e.g. Al toxicity) is therefore bound to progress in the analytical chemistry of ion species of these elements.

The H^+/OH^- buffer systems existing in soils are summarized in fig. 1. For the definition of pH ranges given see ULRICH et al. 1979, ULRICH 1981a, 1983b; the pH given applies to the equilibrium soil solution (ESS) or to $pH(H_2O)$. The buffer reactions given represent the principle, not the true reaction chain. The description holds only for ecosystems being in steady state, unstable ecosystems in transient state may show features of different buffer ranges (e.g. mull in combination with an acid mineral soil). Under the influence of biomass utilization and/or acid deposition the upper soil is often more acidic than deeper horizons. This again is often characteristic for ecosystems in transient state.

There are several aspects of the buffer mechanisms which are especially relevant to resilience. One feature is the limited buffer rate of silicate weathering and release of Al ions from silicates. If the acid load exceeds the buffer rate, the system switches over to the buffer system operating at lower pH, irrespective of buffer capacity left over. It is therefore very typical for highly loaded soils that they are in the iron buffer range as indicated by podzolization and still can posses remarkable stores of unweathered primary silicates and clay minerals. Only $CaCO_3$ and FeOOH show dissolution rates high enough to buffer any possible load as long as the buffer substances are distributed evenly in the fine earth.

Another important feature is the reaction product. Buffering means that a stronger acid is converted to a weaker one. With $CaCO_3$ as buffer the acid formed is carbonic acid, with silicate as buffer silicic acid (or their salts, the clay minerals). Both acids have low solubilities and approach zero solubility in the pH range 7 to 5. Looking at the final reaction products, CO_2 and SiO_2, it becomes obvious that the protons are finally transferred to the weakest acid existing: water. Only these two buffer substances are therefore neutralizing acidity. The release of cation acids below pH 5 indicates that the load exceeds the possible neutralization rate of the system. At early stages of acidification the cation acids released may be completely accumulated in the soil (e.g. as interlayer Al-hydroxy complexes and exchangeable Al ions) and no acidity leaves the system in the output. Soils can behvae like chromatographic columns (in which shortcuts are possible however).

The release of alcali and earth alcali cations from silicates under proton consumption is the only buffering process in the pH range somewhat above 6 (the real value depends on the CO_2 pressure which is variable) and 5.0. The process is not limited to this pH range, however, and may proceed at a somewhat increased rate at lower pH. The increase in the rate is by far not proportional to the increase in H^+ concentration, however; may be a factor of two at the most. From the data

available till now (ULRICH 1981a, JOHNSON et al. 1982, BACHE 1983, MAZZARINO 1983) one can conclude that most soils developed from sedimentary rocks have a buffer rate down to 1 m soil depth of less than 1 keq H^+ ha^{-1} yr^{-1}, whereas higher rates are characteristic for basic magmatic rocks. The ongoing of silicate weathering in acidified soils explains why soils and ecosystems can recover: if the rate of proton load becomes less than the rate of proton buffering by base cation release due to silicate weathering, acidity accumulated in soil is consumed. This means that the amount of cation acids is reduced equivalent to the accumulation of alcali and earth alcali cations (especially Ca and Mg), and the remaining cation acids are transferred to weaker acids (e.g. to a higher polymerization degree in case of Al polymeric ion species).

Fig. 2 demonstrates the role of cation exchange. The exchange of Ca ions against protons is a rapid and reversible reaction. It can be reversed if protons are consumed by some other reaction (e.g. reacting with $CaCO_3$ or by some process in ion uptake or mineralization). The protonized clay, however, is not stable and changes slowly in an irreversible reaction releasing Al ions. The process is temperature dependent and may need weeks to months before taking place to a considerable degree. The cations (Ca) exchanged are leached in combination with the anion of the acid. The cation exchange Ca/H is a very important short term buffer. As long as this reaction runs forth and back, the soil can buffer acidification pushes resulting from a discoupling of the ion cycle in a way very convenient for the organisms: the acid/base status of the soil solution remains almost unchanged, but the nutrient concentration in the soil solution is increased. But the trouble starts if the ecosystem is not capable of shifting the exchange reaction back before the protolysis of the clay starts. Organic cation exchangers, that means a higher store of soil organic matter, reduces this danger and increases therefore considerably the resilience of the system.

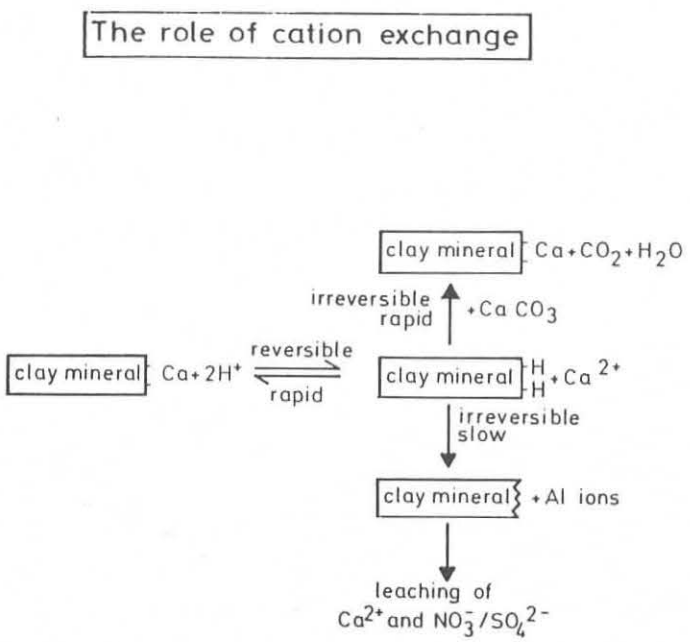


Figure 2.

Discoupling of the ion cycle: Acidification pushes

As a consequence of the relative high optimal temperature of soil microorganisms, soil temperature determines the soil organic matter regime: Low mean soil temperature and a long period with temperatures below 8°C are the base for high soil organic matter stores, whereas the opposite conditions favour mineralization and thus result in low soil organic matter stores in steady state.

Under the conditions of temperature limited decomposition, which are typical for Central and North Europe, a characteristic discoupling of the ion cycle occurs if nitrification hurries on ahead of nitrate uptake. Since nitrification leads to the production of a strong acid (HNO_3), whereas nitrate uptake means the consumption of the same acid, this discoupling leads to an acidification push. In soils with a high percentage of exchangeable Ca, the acidification may show up only in a decrease of exchangeable Ca and an increase of exchangeable H, in soils depleted of exchangeable Ca also pH may be lowered.

Three time spans of discoupling need to be distinguished:

- short term: seasonal discoupling, seasonal acidification push. Especially in spring when the soil is heated up and mineralization starts, but ion uptake is limited before leaf burst; or in autumn after rewetting of a dry soil
- middle term: climatic acidification push.
  In soils in the exchange buffer range (fig. 2), which have already lost considerable fractions of exchangeable Ca, a year or a sequence of years being substantial warmer than the mean can lead to a longer lasting discoupling of the ion cycle by favouring mineralization and nitrification. That a stimulation of microbial activity can be the result of soil acidification has been shown in field and laboratory experiments with acid rain (TAMM et al.1980, HOVLAND et al. 1980, STRAYER et al. 1981, KILLHAM et al. 1983). The discoupling may last for several years, it may be stopped if in cool years mineralization is slowed down and nitrification is depressed to a rate not exceeding nitrate uptake. A climatic acidification push leads always to the release of

Al ions in the soil and the leaching of Ca and NO_3 ions from the root zone.

- long term: humus disintegration.
  If the exchangeable Ca is depleted, the ecosystem may be unable to return to a steady state, that means to close the cycle of mineralization and ion uptake again. In this case the organic matter and the organic nitrogen accumulated in the mineral soil is slowly lost, the process ends if the soil organic matter content approaches low values. It is evident that this process happens, because non-hydromorphic acid soils of stable forest ecosystems show low humus contents in mineral soil whereas soils in the silicate buffer range may have appreciable contents. The last ones are the precursors of the first ones. This process has not been identified and investigated till now, for some ideas how buildup and breakdown of humus are influenced see ULRICH (1981). The process can be followed by balancing input and output: the nitrate output exceeds nitrate input if the process is going on. A soil rich in organic matter with a narrow C/N ratio has a tremendous acidification potential: 14 kg N can produce up to 1 kmol H^+, N stores in soils before passing through humus disintegration may exceed 10 000 kg N/ha.

Acidification effects of biomass utilization

In table 1 the annual uptake rates and ion balances are given for different tree compartments of a beech (Fagus silvatica) stand in the Solling. The tree compartments correspond to different degrees of phytomass utilization: bole (wood + bark), bole + branches, total overstory, total overstory and understory. The cation/anion balance shows that as long as only the woody parts of the overstory are used and exported from the ecosystem, the soil acidification is in a range (0.6 kmol H^+ $ha^{-1}yr^{-1}$) which can be buffered by "better" soils by base cation release during silicate weathering. If the nitrogen rich parts are continuously exported from the ecosystem (e.g. by litter utilization, which played a role during the last centuries), soil acidification increases strongly. Even the utilization of total overstory and understory represents a

realistic picture of some forest areas in Central Europe during the last centuries. All forest soils, where such utilizations have been practisized, have been strongly acidified when modern forestry started.

Table 1: Annual rates of ion uptake in various tree compartments of a beech stand (Fagus silvatica)

	bole	bole + branches	leaves	total overstory + understory
	keq per ha and year			
cation sum	0.69	0.83	1.64	4.34
anion sum	0.11	0.16	0.35	0.83
cation/anion balance	+0.58	+0.67	+1.29	+3.51

Stability and destabilization phases

In fig. 3 a system of stability and destabilization phases is given for non-hydromorphic soils and the post-glacial conditions of Central Europe. This system is based on the buffer ranges shown in fig. 1 and the tendency of soil acidification caused by climatical variation and biomass utilization.

Aggradation phase

The term "aggradation phase" is used here for ecosystems in which the organic matter storage in mineral soil is increasing through accumulation of organic matter with narrow C/N ratio ($\sim$10/1). The humusform is any subtype of mull. With this phase, soil and ecosystem development starts at a freshly exposed surface of loose sedimentary rocks, e.g. after glaciation. As an example a soil may be considered where an amount of 100 000 kg organic matter per ha has been accumulated, the carbon content of organic matter = 50 %, C/N ratio = 10, CEC (cation exchange capacity) = 4 eq/kg C. The CEC indicates a production of 200 kmol H^+ha^{-1}. If the aggradation phase lasts for 1000 years, the mean annual proton production would be 0.2 kmol H^+ ha^{-1} yr^{-1}. This can easily be buffered by silicate weathering and will therefore not result in soil acidification. The N accumulated originates either mainly from N_2 (legumes) or from nitrate input

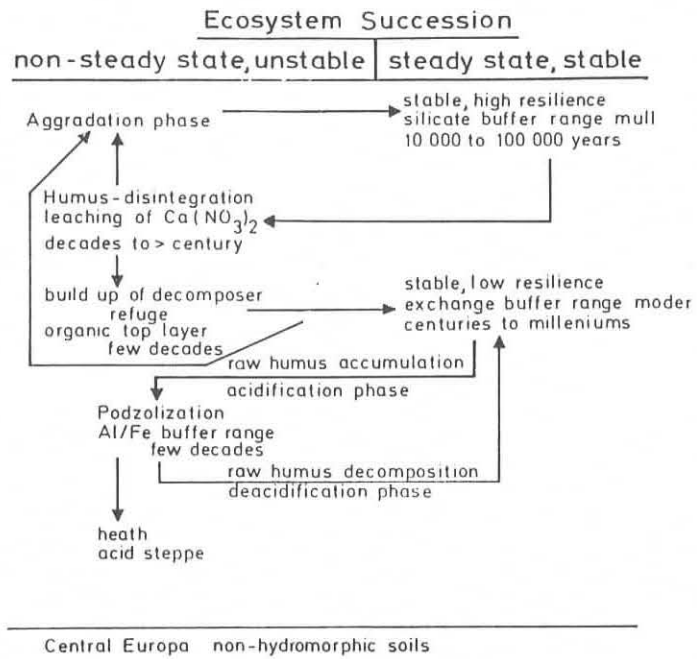


Figure 3.

with rain. Assuming a nitrate input of 4 kg N ha^{-1} yr^{-1} for a period of 1000 years, the nitrate will contribute 40 % of the N accumulated and its transfer to organic bound N will have consumed 286 kmol H^+ ha^{-1}. A small nitrate input, as can be expected under natural conditions, may contribute substantially to the buffering of protons resulting from biomass and soil organic matter accumulation.

Under climatic conditions favouring mineralization the build up of a soil organic matter store will be very limited and may approach zero. The weathering of silicates by carbonic acid will than result in the formation of bicarbonates, that means that the soil starts to accumulate basicity. As long as precipitation exceeds evapotranspiration, this basicity can be leached and the soil remains "neutral", that is in pH range 5 to 6. If, however, evapotranspiration exceeds precipitation, the consequence will be the alcalinization of the soil. Long term agriculture is therefore only possible under the condition that precipitation + irrigation exceeds evapotranspiration.

Stability with high resilience (Stability range I)

If the soil organic matter accumulation has reached a steady state (constant store), the aggrading system passes over into a stable system with high resilience. The soil can stay either in the carbonate buffer range or in the silicate buffer range, so two different states have to be distinguished. The absence of toxic cation acids allows all species of primary producers and of secondary producers (decomposers and consumers) to exist and thus to compete with each other. For the climatical and hydrological conditions given one should therefore expect the greatest diversity, compared with ecosystems on acidified soils. The absence of toxic cation acids means further that roots tend to maximize the contact with soil material where water and nutrients are stored, and that bacteria play the dominant role in the decomposers.

A stable forest ecosystem with high resilience (stability range I) should therefore, under the conditions of Central Europe, being characterized by the following properties:

- it is composed of relatively many species, which are structured in layers
- the soil is deeply rooted, the roots are homogeniously distributed
- the decomposers are characterized by the activity of earth worms
- the soil stays throughout in the silicate (or carbonate) buffer range and shows no depth gradient in the chemical soil state
- soil organic matter is accumulated throughout the whole rooting zone, due to the activity of soil burrowing animals, the soil is of crumby structure.

Examples can be found which demonstrate that untouched forest ecosystems in Central Europe would exhibit these properties.

In the higher altitudes of the subalpine mountains it is possible that a biological depth gradient exists in soil due to frost action. This should result in the formation of an organic top layer which is colonized mainly by arthropods, whereas the mineral soil can still be characterized by earthworm activity. The biological depth gradient implies a chemical depth gradient, that is the organic top layer is more acid than the mineral soil. The climatical limitations to decomposers should thus lower the resilience of the ecosystem - forest ecosystems in higher altitudes or farer north are more easily subjected to plastic strain by climatic or man-made stress.

Even in ecosystems with the soil staying in the silicate buffer range, there is some loss of cations (mainly Ca^{2+}), accompanied by HCO_3^-. This leaching from soil is responsible for the salt content of soft groundwater. In order to keep the ecosystem stable, this loss has to be balanced by silicate weathering. A long-lasting discoupling of the ion cycle is to be expected if, in the course of natural ecosystem development, the weatherable silicates in the root zone are exhausted. If the output (leaching) of Ca and Mg becomes larger than the input (from atmosphere and by weathering), the ecosystem passes over into a nonstationary transition state which is characterized by decreasing stores of exchangeable Ca and Mg. The soil acidifies, the chemical soil state passes over from the silicate

into the cation exchange buffer range. The time span needed for this process can be estimated from the buffer capacity and the buffer rate in the silicate buffer range of the soil. With the values given in fig. 1 (cf. ULRICH 1983b), the buffer capacity amounts to 750 keq ha^{-1} m^{-1} per 1 % silicate content in the soil. With the buffer rate of 0.4 kmol H^+ ha^{-1} yr^{-1} for 1 m soil depth, found by MAZZARINO (1983) for a soil of the last interglaciation period (soil "Dasburg"), a silicate content of 1 % would last for around 2000 years. If this buffer rate is accepted as typical for the natural development of untouched ecosystems on comparable soils in an interglaciation period, it means that soils with silicate contents above 5 % would still be in the silicate buffer range or swinging between silicate and cation exchange buffer range, provided that there was no acidifying influence by man's activities. With a silicate content of 50 % in the parent rock the ecosystem may stay for 100 000 years in this stability range. During this period the lithospheric environment of the ecosystem changes slowly by the transfer of primary silicates into secondary clay minerals. As long as the weathering rate of the silicates remains constant, this will increase the resilience of the system by enlarging the exchangeable Ca+Mg stores.

Phase of humus disintegration (destabilization phase I)

A very long lasting discoupling of the ion cycle should result in the loss of the organic matter which was accumulated in the whole rooting zone, including the subsoil, during the aggradation phase and which was kept on a constant level during the stability range I. This type of discoupling is called humus disintegration (ULRICH 1980). The ecosystem is in a non-stationary transition state which is necessarily limited in time. The time period under question may be decades to centuries, however.

As an example we consider the same soil as before. We assume that the total soil organic matter is mineralized, the nitrogen being nitrified. Denitrification is assumed to be zero. In such a case, there would be a proton consumption by mineralization of the Ca saturated acidic groups amounting to 200 kmol/ha. On

the other hand, nitrification produces 360 kmol H^+/ha. The balance of both partial processes yields a proton production of 160 kmol H^+/ha.

If one assumes that this process takes place within 100 years, the mean annual rate would be 1.6 kmol H^+/ha. This exceeds for many soils the possible buffer rate in the silicate buffer range, thus increasing soil acidity. Existing data indicate that in the early stages of humus disintegration N rich compounds are mineralized preferably. This leads to an increase in the C/N ratio of the remaining soil organic matter. Probably humus disintegration increases also the mobility of the clay and can thus lead to clay migration (~~leesivation~~) in the soil.

Under natural conditions this process seems to be bound to strong climate changes which leads to the destruction of the forest ecosystem. Examples are the changes from interglacial to glacial periods. The destruction of the forest ecosystem by man may trigger the same process. Sustained damage to primary producers is also caused by man. Clear cutting, grazing and shifting agriculture, may result in sustained reduced primary production and even more, in sustained reduction of understory root and overstory leaf etc. litter. It further changes the microclimate of the soil, that is the climatical conditions for the decomposers. Both effects, the reduction in litter production and the increase in soil temperature, operate in the direction of lowering organic matter stores in the mineral soil. They may thus initiate humus disintegration. The process can be started by the acidity produced (alcalinity not returned) by the discoupling of the ion cycle due to biomass utilization.

One should assume that all forest ecosystems in Central Europe have passed after the last glaciation period through the aggradation phase and reached the stability range I. With the exception of parent material very low in silicate content, and of shallow soils, most forest ecosystems should still be in stability range I. This is not the case. Most forest subsoils are in the cation exchange or aluminium buffer range, they show no activity of soil burrowing animals, and the roots are

inhomogeneously distributed. These soils must be assumed to have passed through the phase of humus disintegration centuries or millenniums ago. It must further be assumed that in most cases this process has been initiated by biomass utilization through man.

It seems that in Central Europe all forest ecosystems which have not been subjected to humus disintegration before, have now switched over into this phase. There is no actual reason for this than acid deposition. Acid deposition buffered at the leaf surface is transferred to the soil close to the roots via the regulation of ion uptake (ULRICH 1983a). Acid deposition is therefore especially suited for acidifying the soil in the deeper rooting zone. After a reduction of exchangeable Ca, this may in combination with a climatic acidification push initiate humus disintegration and prevent the process to be stopped again.

In the beginning stages of humus disintegration, the ecosystem resembles the stable ecosystem in the silicate buffer range with the exception of low pH values especially in the deeper rooting zone: the humusform can be still mull, the rooting deep reaching and being homogeneous, the soil structure crumb-like. Due to the continuous surplus of nitrification compared to nitrate uptake, tree growth may be excellent and in the shrub and herb layer plants indicating high nitrogen supply appear. The Al ions released from clay minerals are bound to soil organic matter; this reduces their toxicity. The feature typical for the process running in the deeper rooting zone is the leaching of nitrate in combination with Ca and Mg. The leaching of nitrate indicates the continuous net nitrification (i.e. formation of HNO_3) in the rooting zone. The leaching of Ca and Mg indicates the acidification, i.e. the loss of basic cations and their replacement by Mn and Al ions (i.e. cation acids). The process of humus disintegration can be stopped at any point, if the rate of proton load (HNO_3 formed exceeding HNO_3 uptake + acid deposition) becomes smaller than the rate of proton consumption by base cation release during silicate weathering. That this is reached under the influence of acid deposition is very improbable, however. Also liming may be ineffective, if

not the earthworm activity is high enough to transport substantial amounts of buffering substances down to the subsoil.

Due to its long duration and the excellent growth of Al tolerant tree species, the process is very difficult to recognize and nobody is aware of its dramatic end: the change of the chemical soil state into the aluminium and iron buffer range with all of its consequences for plant growth and decomposer activity. Many stands showing fir die-back seem to be subjected to humus disintegration (ULRICH 1981b). The same seems to be the case with some forest stands in the subalpine mountains.

Destabilization phase II: Build up of a decomposer refuge

If soil acidification has lead to cation acid toxicity to such a degree that bacterial activity in the soil is strongly limited (except in the rhizosphere and the interior of dead roots), also soil burrowing animals are missing and the ecosystem tends to carry through litter decomposition in a top organic layer separated from mineral soil. The lower part of top organic layer may be rooted. In this case not only leaf but also root litter contributes to its formation. The accumulation of a top organic layer means in its essence the build up of a decomposer refuge after the mineral soil has become toxic by the presence of cation acids. It is accompanied by the loss of ground vegetation and started by the retardation of leaf litter decomposition. As a consequence, a fermentation layer (OF horizon) is forming (humusform: F-mull). If the OF increases and roots are stretching between OF and A horizon, the accumulation of a well decomposed OH horizon starts (humusform: mull-like moder). The accumulation can be stopped at any stage, provided that the conditions for decomposers allow to carry through decomposition and mineralization at the same rate as litter production (reaching of a steady state). This is usually achieved after developing a full OL-OF-OH profile (humusform: moder). The mineral soil, at least its uppermost horizons, stay in the aluminum buffer range or swing between exchanger buffer range and Al buffer range.

The build up of an organic top layer is accompanied by a proton production in the root zone. For the beech ecosystem taken as an example the rate of proton production can be estimated from the data presented in table 1. If litter decomposition is completely stopped, the proton production in soil corresponds to the cation/anion balance of the leaf litter and would amount to 1.3 kmol H^+ ha^{-1} yr^{-1}. All values between zero and this maximum value are possible, depending upon the fraction of litter which is accumulated. This means that the ecosystem can again reach a steady state, characterized by an acid soil and moder as humusform. The system can, however, also switch over to podzolization, if the buffer rate in the Al buffer range is to small compared to the proton production, the proton buffering will than be taken over by iron oxides.

Stability with low resilience: Stability range II

As soon as the mineralization rate approaches the rate of litter production, proton production ceases and the ecosystem can again reach a quasi-steady state. The chemical soil state may then slowly pass back to the cation exchange buffer range. The rate of this recovery process depends upon the rate of proton consumption by silicate weathering (base cation release): by this process cation acids are transferred to uncharged compounds and base cations produced, so the percentage of exchangeable Ca+Mg can slowly increase. Finally a steady state may be achieved where the base cation percentage fluctuates around a mean value corresponding to the effects of climatic acidification pushes and deacidification phases.

This stability range is characterized by a much lower resilience than stability range I with the soil staying in the silicate buffer range. The missing of soil burrowing animals has the consequence that within the soil compartments develop with different chemical state: Between these compartments chemical gradients exist. Such compartments are the organic top layer and the mineral soil, the different horizons within these layers, and the interior and surface of aggregates within these horizons.

The extention of roots into the organic top layer may be of great advantage to avoid spatial discoupling of proton production and proton consumption, but makes the plants susceptible to drought periods. Within the mineral soil,the roots are growing along the surface of aggregates. The humic substances formed during root decomposition are therefore accumulating at the aggregate surfaces close to the roots and are not mixed within the total soil mass. This increases considerably the risk for cation acid (Al) toxicity in case of a strong seasonal acidification push: The nitric acid forms in a very small soil volume only which is close to the roots. In this small soil volume the buffer capacity is very limited. The frequency of the formation of toxic cation acids injuring microorganisms and roots can therefore vary considerably between ecosystems.

Most forest ecosystems in Central Europe have passed through humus disintegration and build up of a decomposer refuge centuries or milleniums ago and should be in this stability range with the soil staying somewhere in the cation exchange buffer range. They are almost all subjected to biomass utilization by modern forestry. As discussed already the proton production caused by bole utilization in the beech ecosystem under consideration amounts to 0.6 kmol H^+ ha^{-1} yr^{-1}. In most forest ecosystems this internal proton load may be balanced by silicate weathering. This means that these ecosystems can maintain in a steady state under the influence of biomass utilization in case of careful forest management. But it can also be that silicate weathering cannot buffer the acidification effect of biomass utilization. This can be checked by long term cation/anion balances. If it is the case, the ecosystem will change slowly during tree generations with the productivity going back. It seems that such cases are widespread but hidden due to the overwhelming influence of acid deposition.

In any case, there is in most managed forest ecosystems no buffer ability by silicate weathering left to neutralize acid deposition. This means that acid deposition decreases first the resilience and than destabilizeses almost all forest ecosystems. The higher the rate of acid deposition, the faster the effects

will show up. But it is to be expected that even low rates of acid input lead finally to the destabilization of the forest ecosystem. It is our responsibility, here and now, to cut down the emission of acid forming gases.

Phase of podzolization

Podzolization is usually considered as a soil process, but it is in its essence an ecosystem process. The source of the protons is again the discoupling of the ion cycle by accumulating litter and litter residues on top of the mineralsoil. The difference to the phase of build up of a decomposer refuge is just that the soil stays in the iron buffer range. Due to the presence of stronger acids the stress to the trees may be stronger than in the Al buffer range. Since the proton production is bound to the accumulation of the organic top layer, podzolization ceases if the organic top layer reaches a steady state. One should therefore carefully distinguish between active and inactive podzols, the last ones shows the features of podzolization (greyish A horizons and accumulation of iron and organic matter in a deeper horizon) but the process is not going on. It seems that acid tolerant trees (like Norway spruce and Scots pine) can withstand the high acid strength existing during podzolization for a limited time period, around two decades probably. If the process than stops the trees will survive and the forest cover remains. This is the time span which the build up of a decomposer refuge needs on a strong acidified soil and is thus what the trees have experienced during evolution. If due to the action of man, may be by utilizing biomass, by founding plantations or by acid deposition, the active podzolization continues over longer periods of time, the trees will die back and the forest is changed into some other ecosystem, e.g. into a heath. Incipient podzolization (bleaching without a B horizon) is now very common in Central European forests as a consequence of acid deposition. If acid deposition continues, the forest will die back sooner or later. There is no way out except the cut down of acid deposition.

Resilience due to organisms

The problem of tree die back on acid soils leads back to the resilience of the ecosystem. As already stated, the main weight of buffering lies on the soil and not on the organisms. This is especially true for ecosystems of high diversity in the stability phase I. In ecosystems on acid soils, however, organisms have an own ability to buffer acidity. The acidity appears in the form of cation acids and we speak about tolerance against manganese and aluminium toxicity. From an ecosystem point of view the mechanisms acting first in case of an acid stress are located in the soil. If these mechanisms are overstressed, they produce cation acids. Now the rhizosphere and the mycorrhiza become involved. If they cannot maintain neutrality and become injured, the acid soil solution can enter the free space of the root cortex. In this case the apoplasm comes into play, it may possess a substantial buffer capacity in the form of Ca ions bound to acidic groups in the cell wall. The tolerance mechanisms can make use of three types of chemical reactions:

- cation exchange: the cation acids are bound to surfaces, in the solution they are replaced by the Ca exchanged,
  restriction: limited buffer capacity
- precipitation of cation acids, e.g. as phosphates or silicates.
  restriction: limited resource of anions, P deficiency
- precipitation of cation acids as hydroxides, partially in the cortex.
  restriction: limited resource of basicity in an acid environment
- chelation of cation acids: the formation of metal-organic compounds masks the toxic ion. If the complexes are stable enough they may pass through the symplasm without making harm.

Acid tolerant tree species seem to be able to protect the symplasm very effectively. Their problem is, however, the acidification of the apoplasm. BAUCH et al. (1982) have shown

that injured roots of Abies alba (fir) and Picea abies (Norway spruce) have lost Ca and Mg from the cortex whereas Al is present. In diseased spruce trees the cell wall of the cortex and primary xylem did'nt contain Ca and only small amounts of Mg. The average concentration of Al was lower than in the control from healthy trees. From a chemical point of view this is to be expected if the solution in equilibrium with the cation exchanger approaches pH values around 4.2: the dissociation of the acidic groups in the cell wall goes back, thus limiting the exchange capacity; Ca and Mg are completely displaced from the exchanger surface; and polymeric Al ions are transferred to Al^{3+}, thus increasing the charge of the Al ions and decreasing the amount of Al which can be bound at the exchanger surface. TISCHNER et al. (1983) show with spruce seedlings that under these conditions the cortex becomes separated from the xylem and the formation of the endodermis is disturbed.

A further important mechanisms for acid tolerant species to increase resilience is the regeneration of injured roots. This ability may become limited the more cation acids penetrate also into older roots so that finally the whole root system may be acidified.

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